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Dielectric Properties of (Cellulose Oligo-Oxymethylene Ether) Acylates

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Abstract—The dielectric properties of (cellulose oligo-oxymethylene ether) acylates were measured over a wide frequency and temperature range. The resulting complex dielectric constants (ϵ^*) were found to be closely related to complex dynamic modulus (E^*) in the region of the mechanical β and γ processes through the following expression:

$$(\epsilon^* - \epsilon_U)/(\epsilon_R - \epsilon_U) = 1 - (E^* - E_R)/(E_U - E_R)$$

where ϵ_R and ϵ_U are the relaxed and unrelaxed dielectric constant, while E_R and E_U are the relaxed and unrelaxed dynamic modulus. From this, we used the dielectric relaxation data for discussing the β and γ processes so far detected by mechanical experiment. In the dielectric measurement at constant temperatures, the γ absorption for the acetate exhibited a marked peak, while the β absorption appeared as a low frequency shoulder to the γ peak. The normalized absorption curves for the γ process in the acetate at temperatures between -70°C and 0°C reduced to a single curve (master curve). However, the absorption curves below -80°C deviated from the master curve, but instead, they were on the master curve for the pivalate. In accord with this, the plots of $(\epsilon_R - \epsilon_U)$ vs. temperature in the γ region for the acetate changed sharply at about -80°C . From these findings, the molecular relaxation mechanism for the γ process in the acetate was considered to be different below and above ca. -80°C . The similar results were drawn for other COAs with linear side chain. It was also shown that the β process gave unexpectedly large values of the activation entropy (100eu or more), and the process was confirmed to be due to the micro-Brownian motion of the side chain.

Introduction

In our previous work, we studied the viscoelastic properties of polymers in a series of (cellulose oligo-oxymethylene ether) acylates, COAs, using dynamic mechanical measurements¹⁻³⁾. The five types of relaxation processes were observed, though their occurrence depended on the kind of COAs. They were respectively attributed to: micro-Brownian motion of the main chain (α), micro-Brownian motion of side chain (β), local mode motion involving oxymethylene group (γ), motion initiated by three or more methylene groups (δ), and motion of two methylene groups (δ'). Of the five, we are particularly interested in the presence of the γ and

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β processes because these two are characteristic for COAs. Thus, further information on these two processes is desirable to understand various physical properties of COAs. However, our knowledge on molecular mechanism of these relaxation is restricted, as far as we use mechanical measurement, because such measurement generally gives data only in narrow frequency range, although they span wide temperature range.

On the other hand, observation of relaxation processes can be made over a wide frequency and temperature range by using dielectric measurements. Thus, if respective dielectric relaxation processes measured correspond well with mechanical one, then the dielectric measurement could be used for compensating mechanical measurement.

In our present work, we firstly clarify the relation of dielectric relaxation to dynamic mechanical one for COAs. Then, we obtain further information on the β and γ processes through dielectric experiments over a wide frequency and temperature range.

Experimental

Samples

The COAs used were the acetate (CAcOM), propionate (CPrOM), butyrate (CBuOM), valerate (CVaOM), pivalate (CPiOM), and decanoate (CDeOM). Their preparing procedures were the same as in our previous report¹⁾. The dissolution condition of cellulose in paraformaldehyde/dimethylsulfoxide medium was 120°C for 3 hrs.

Measurement of dynamic mechanical properties

A direct reading viscoelastometer (Toyo Baldwin Co., Ltd., Rheovibron DDV-II-C) was used in the same manner as in our previous report¹⁾. Complex modulus and loss tangent were measured in the temperature range from -190°C to 20°C at a frequency of 110 Hz. The programmed heating rate was about 1°C/min.

Measurement of dielectric properties

Using a transformer bridge (Ando Denki, TR-10C), dielectric constant and dielectric loss were measured over the frequency range of 30 Hz to 1 MHz and the temperature range of -190°C to 50°C.

Results and Discussion

Prior to discussing the dielectric relaxation processes for COAs, we examine the relationship between dynamic modulus E' and dielectric constant ϵ' , or between loss modulus E'' and dielectric loss ϵ'' using their normalized form defined as

$$\begin{aligned}
 \tilde{E}' &= 1 - (E' - E_R) / (E_U - E_R) \\
 \tilde{\epsilon}' &= (\epsilon' - \epsilon_U) / (\epsilon_R - \epsilon_U) \\
 \tilde{E}'' &= E'' / E''_{\max} \\
 \tilde{\epsilon}'' &= \epsilon'' / \epsilon''_{\max}
 \end{aligned}
 \tag{1}$$

where the values with subscript R are chosen at the temperature at which the relaxation completed, while the values with subscript U are chosen at the temperature at which the relaxation apparently set in. The temperature dependence of thus defined $\tilde{\epsilon}'$ and \tilde{E}' , or that of $\tilde{\epsilon}''$ and \tilde{E}'' at 110 Hz for CAcOM are shown in Figures 1a, b in the β and γ regions. Apparently, the $\tilde{\epsilon}'$ and $\tilde{\epsilon}''$ values are respectively in good agreement with the \tilde{E}' and \tilde{E}'' values in the range examined. Also, the same results are observed in Figures 2a, b for CPiOM in which only the γ region appears below room temperature.

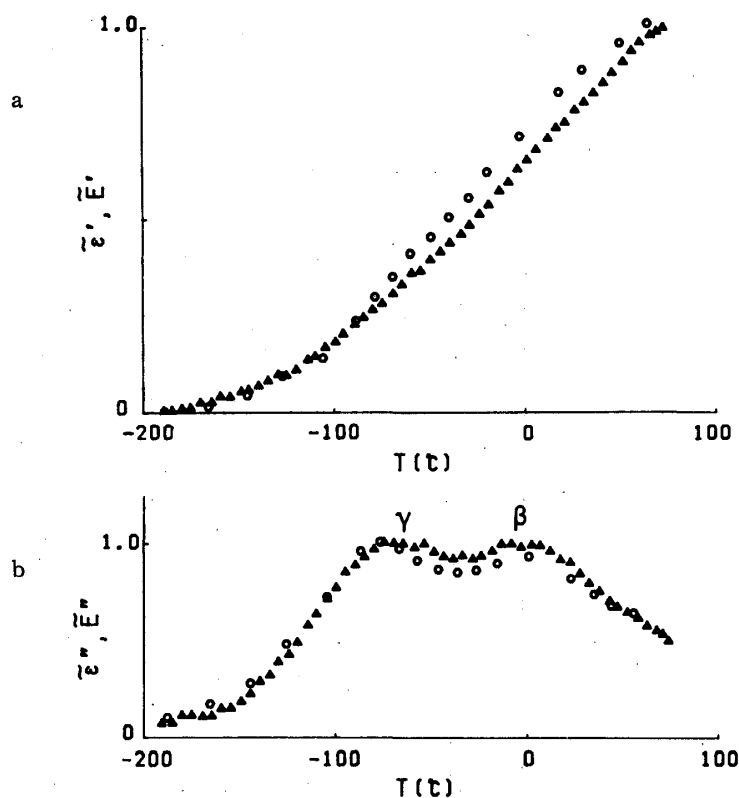


Fig. 1a, b. Temperature dependence of $\tilde{\epsilon}'$ and \tilde{E}' , or that of $\tilde{\epsilon}''$ and \tilde{E}'' at 110 Hz for (cellulose oligo-oxymethylene ether) acetate, CAcOM. $\tilde{\epsilon}'$, $\tilde{\epsilon}''$: \circ , \tilde{E}' , \tilde{E}'' : \blacktriangle .

However, for the higher homologue above CBuOM, such comparison of $\tilde{\epsilon}'$ with \tilde{E}' or $\tilde{\epsilon}''$ with \tilde{E}'' becomes invalid in the region of the δ process which appears in a lower temperature in addition to the β and γ processes. Figures 3a, b, c, and d respectively show temperature dependence of ϵ' , ϵ'' , E' , and E'' at 110 Hz for

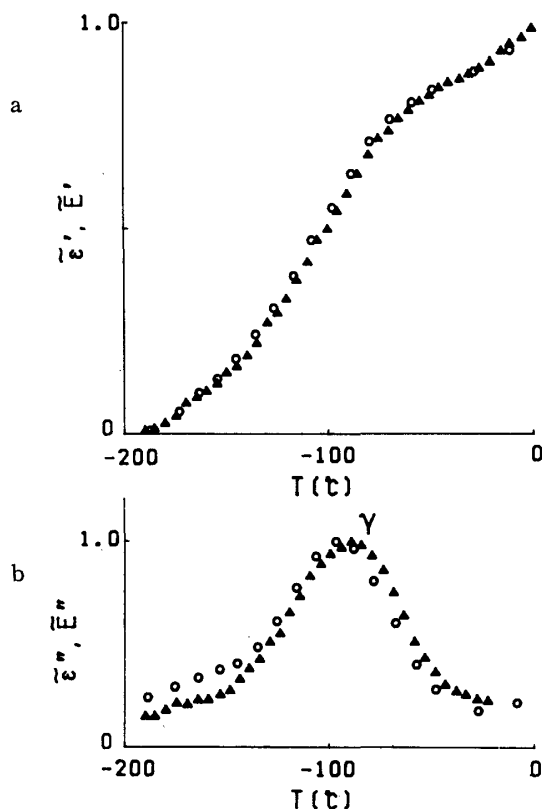


Fig. 2a, b. Temperature dependence of ϵ' and \tilde{E}' , or that of ϵ'' and \tilde{E}'' at 110 Hz for (cellulose oligo-oxymethylene ether) pivalate, CPiOM. ϵ' , ϵ'' : ○, \tilde{E}' , \tilde{E}'' : ▲

CDeOM in the range of β to δ processes. Regarding mechanical data (Fig. 3c, d), it is evident that the δ process exhibits a marked peak in E'' curve and a large change in E' curve. On the other hand, the corresponding dielectric process (Fig. 3a, b) appears only as a shoulder in ϵ'' curve in somewhat higher temperature range, being associated with little change in ϵ' . It is of interest to note, however, that when ϵ'' curve is normalized in the range of the β and γ processes except for the δ region, the dielectric data corresponds again to the mechanical one as shown in Figure 4 for $\tilde{\epsilon}'$ and \tilde{E}' . From these results, we find that the relationship between \tilde{E}' and $\tilde{\epsilon}'$, or \tilde{E}'' and $\tilde{\epsilon}''$ can be expressed as

$$\tilde{E}' = \tilde{\epsilon}', \quad \tilde{E}'' = \tilde{\epsilon}'' \quad (2)$$

in the β and γ regions for COA. By using complex modulus E^* , and complex dielectric constant ϵ^* defined as $E^* = E' + iE''$, $\epsilon^* = \epsilon' + i\epsilon''$, the expression (2) reduces to

$$1 - (E^* - E_R)/(E_U - E_R) = (\epsilon^* - \epsilon_U)/(\epsilon_R - \epsilon_U) \quad (3)$$

in making reference to the expression (1). On the other hand, E^* and ϵ^* can be expressed in terms of normalized relaxation spectra H and ϕ , respectively:

$$E^* = E_R + (E_U - E_R) \frac{H(\tau_0, \Delta E) i \omega \tau_0 e^{\Delta E/kT}}{1 + i \omega \tau_0 e^{\Delta E/kT}} d\tau_0 d\Delta E$$

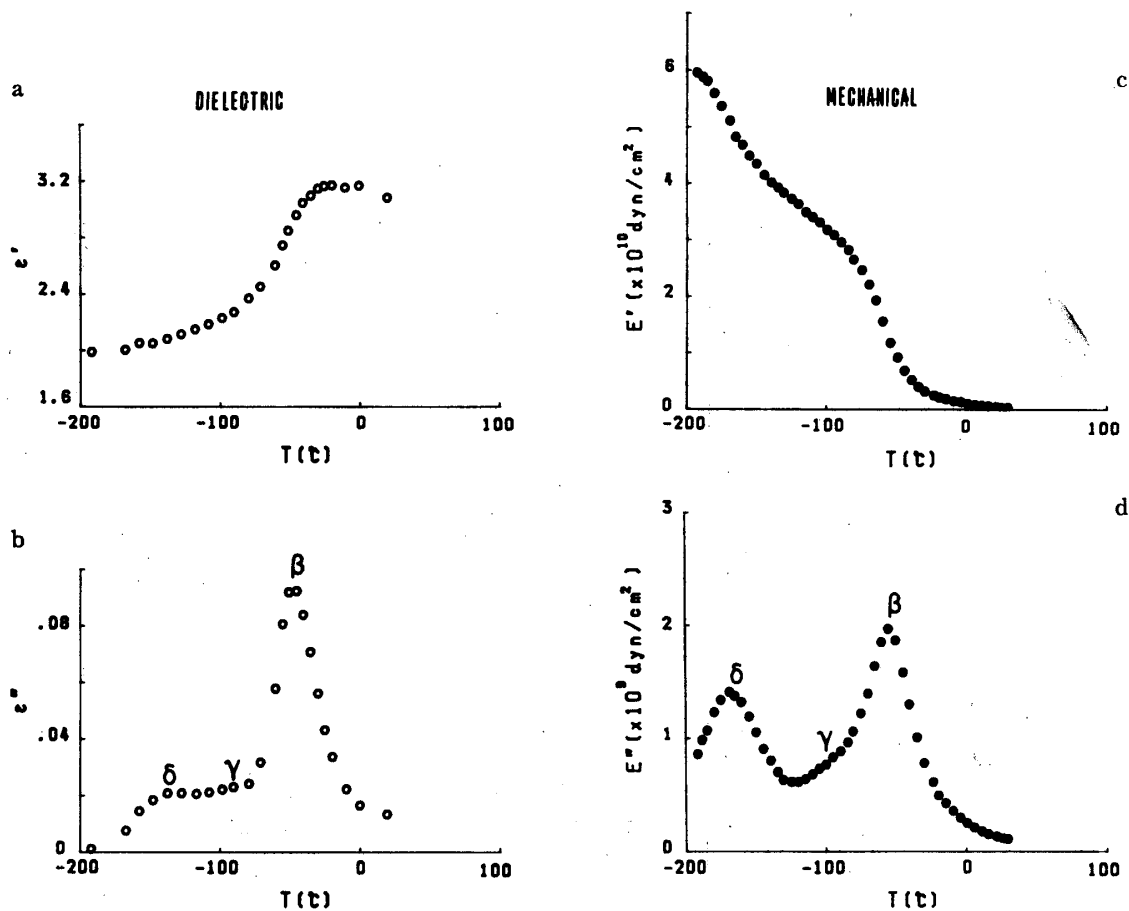


Fig. 3a, b, c, d. Temperature dependence of ϵ' , ϵ'' , E' , and E'' at 110 Hz for (cellulose oligo-oxymethylene ether) decanoate, CDeOM.

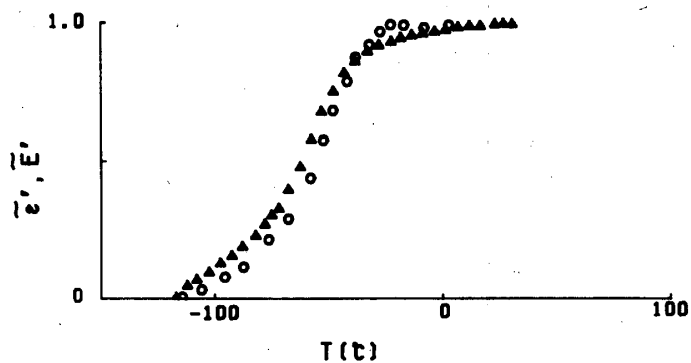


Fig. 4. Temperature dependence of ϵ' , and E' at 110 Hz for (cellulose oligo-oxymethylene ether) decanoate, CDeOM, above -120°C . ϵ' : \circ , E' : \blacktriangle .

$$\varepsilon^* = \varepsilon_U + (\varepsilon_R - \varepsilon_U) \frac{\phi(\tau_0, \Delta E)}{1 + i\omega\tau_0 e^{\Delta E/kT}} d\tau_0 d\Delta E \quad (4)$$

where τ_0 : relaxation time at high temperature

ΔE : apparent activation energy

T : temperature

R : gas constant

ω : angular frequency

Substitution of Eq (4) to Eq (3) yields

$$H(\tau_0, \Delta E) = \phi(\tau_0, \Delta E).$$

This further reduces to

$$H(\tau) = \phi(\tau),$$

where $\tau = \tau_0 \exp(\Delta E/RT)$

Therefore, the dielectric relaxation data for COAs in the β and γ region can be regarded essentially as equivalent to the mechanical one.

In the following, the γ and β processes so far detected by the mechanical measurement are discussed in detail using the results of dielectric measurement at a constant frequency over a wide frequency and temperature range. Figure 5 displays plots of ε'' against logarithmic frequency (absorption curve) for CAcOM measured at temperatures from -190°C to -2°C . From the figure, it can be seen that a relaxation process appears as a peak above -90°C . Since the relaxation region recognized here continuously moves to the γ region observed from the mechanical

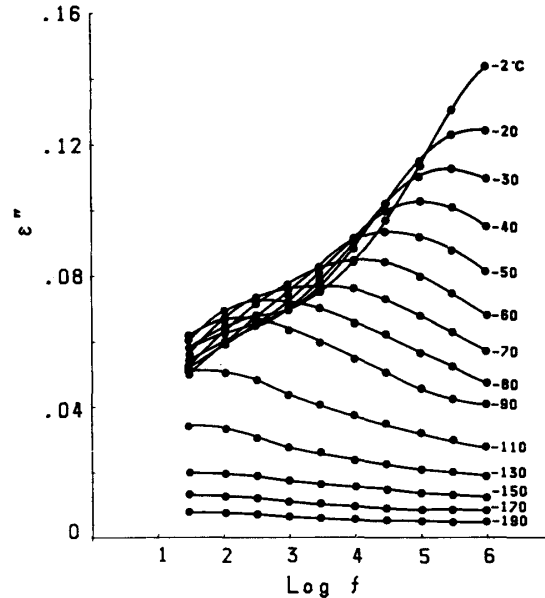


Fig. 5. Frequency dependence of ε'' at temperatures between -2°C and -190°C for (cellulose oligo-oxymethylene ether) acetate, CAcOM, in the β and γ regions.

measurement at a constant low frequency, this relaxation is classified as the γ process. On the other hand, in the temperature range -20°C to -2°C another relaxation is observed as a low frequency shoulder to the γ peak. In the same manner, this relaxation is considered to be the β process. Remember here that for CAcOM the β and γ regions observed from constant frequency experiment at a low frequency (Fig. 1b) overlapped, and formed double peaks, each of which is similar in height. Evidently, however, Figure 5 gives a predominant γ peak which is little affected by the β process.

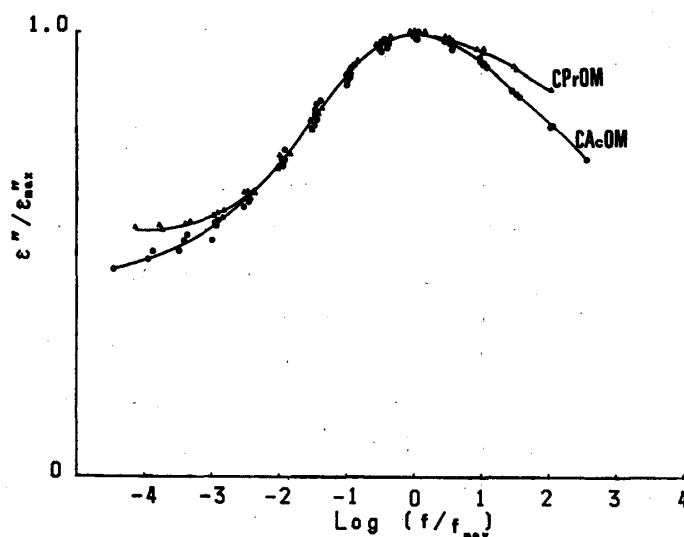


Fig. 6. Superposition of $\epsilon''/\epsilon''_{\max}$ vs. $\log f/f_{\max}$ for the γ process of CAcOM and CPrOM.

For the γ process in CAcOM, an attempt was made to construct a reduced master curve (normalized absorption curve) from plots of $\epsilon''/\epsilon''_{\max}$ vs. $\log(f/f_{\max})$ at temperatures from -70°C to -2°C , and the results are shown in Figure 6. In the figure, the results for the γ process in CPrOM are also plotted. It can be seen that the plots for CAcOM and CPrOM are reduced to a single curve within the $\log(f/f_{\max})$ range between -2.5 and 0 . However, the curves separate out the range: the slope for CPrOM is smaller than that for CAcOM. The increase in absorption for CPrOM in higher frequency side arises from the presence of the δ' process due to motions of $-\text{CH}_2-\text{CH}_2-$ parts in the side chain, i.e., perturbation mode of the $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ motion (δ process). Similar contribution caused by $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ motion to the slope in higher frequency is observed in higher homologue of COAs with linear side chain. Since absorption curve for CAcOM do not include such relaxation, its slope in higher frequency can be considered to be an essential characteristic of the γ process. Therefore, the curve in the range above $\log(f/f_{\max}) =$

—2.5 for CAcOM can be thought to give master curve of the γ process for COAs. However, since plots for CAcOM below -80°C were not on the master curve, they were omitted in the figure. This point is discussed in later paragraph in relation to the absorption curve for CPiOM. On the other hand, the splitting of the curve in lower frequency tail results from the different contribution of the β process which appears as a low frequency shoulder to the γ peak. Accordingly, even for CAcOM the absorption curve in this range is considered to be modified by the β process.

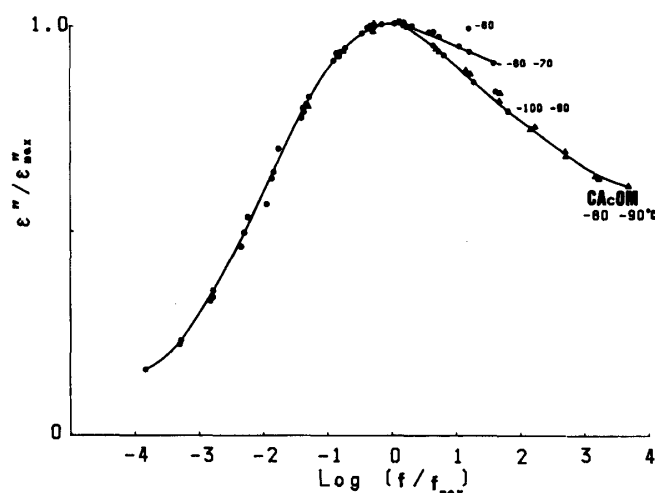


Fig. 7. Superposition of $\epsilon''/\epsilon''_{\max}$ vs. $\log f/f_{\max}$ for the γ process of CPiOM.

Figure 7 illustrates normalized absorption curve at temperatures from -100°C to -60°C for the γ process in CPiOM whose β process is known to appear in the frequency temperature ranges far removed from those of the γ process. It can be seen that the resulting plots below $\log(f/f_{\max})=0$ are on a single curve, and its shape in lower frequency is considerably sharp as compared with that for CAcOM or CPrOM shown in Figure 6. Since for CPiOM the β process is not involved in this region, the shape of the curve in this region can be regarded as essential for the γ process of CPiOM. On the other hand, above $\log(f/f_{\max})=0$ the splitting of the curve is observed: the slope of the higher frequency side becomes milder with increasing temperature. This is due to the increase of the contribution of the δ' process to the higher frequency side of the γ process, because the γ region moves to more rapidly than the δ' region, and so the latter is included more and more with increasing temperature. Therefore, the curve including plots at -80°C and -90°C is most reliable as the master curve for the γ process in CPiOM. It is of interest to note that the width of the master curve for the γ process in CPiOM seems narrower than those for CAcOM. Furthermore, plots for CAcOM below -80°C which

were omitted in Figure 6 are on the master curve in CPiOM as shown in the figure. These findings suggest different relaxation mechanism for the γ process between CPiOM and other COAs (including CAcOM) with linear side chain.

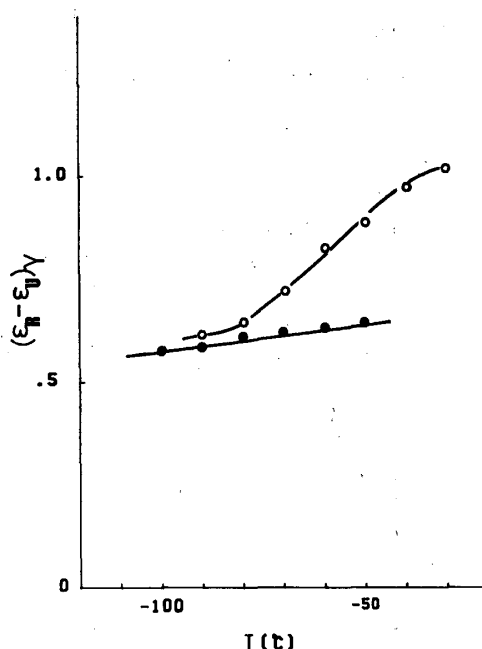


Fig. 8. Temperature dependence of $(\epsilon_R - \epsilon_U)_{\gamma}$ for CAcOM (○) and CPiOM (●).

In order to clarify this point, Figure 8 shows the relaxation magnitude of the γ process, $(\epsilon_R - \epsilon_U)_{\gamma}$ for both CPiOM and CAcOM calculated from cole-cole's circular arc plots. With increasing temperature up to -80°C , the values of $(\epsilon_R - \epsilon_U)_{\gamma}$ increases slightly for both CPiOM and CAcOM but above -80°C markedly for CAcOM. This phenomenon for CAcOM is called dielectric transition, indicating the difference in relaxation mechanism for the γ process above and below ca. -80°C . Remember here that the micro-Brownian motion along the side chain responsible for the β process is released in the temperature range just above the γ region for COAs with linear side chain such as CAcOM, while for CPiOM it occurs at a temperature range substantially higher than that of the γ process. Therefore, if the micro-Brownian motion along the side chain for CAcOM is released at about -80°C , motion of oxymethylene groups above -80°C (the γ process) is affected to some extent by such motion. This situation is thought to be reflected as dielectric transition in the γ region for CAcOM. Such being the case, the γ absorption curve below -80°C for CAcOM agrees with that for CPiOM in which no segmental motion in the side chain is involved in the γ region.

Regarding the γ process, transition map (Arrhenius plots) for CAcOM, CPrOM,

and CPiOM determined by frequency dispersion data is shown in Figure 9a, and that for CPiOM obtained by temperature dispersion data is shown in Figure 9b. The values of activation energy ΔE , entropy ΔS , and free energy ΔF calculated from these plots are also shown in the figures. From these figures, the γ process is found to occur in a similar frequency and temperature region regardless of both the kind of COAs and the measuring processes. In this connection, the mechanical data reported previously³⁾ at a constant frequency are on the line in Figure 9b. These

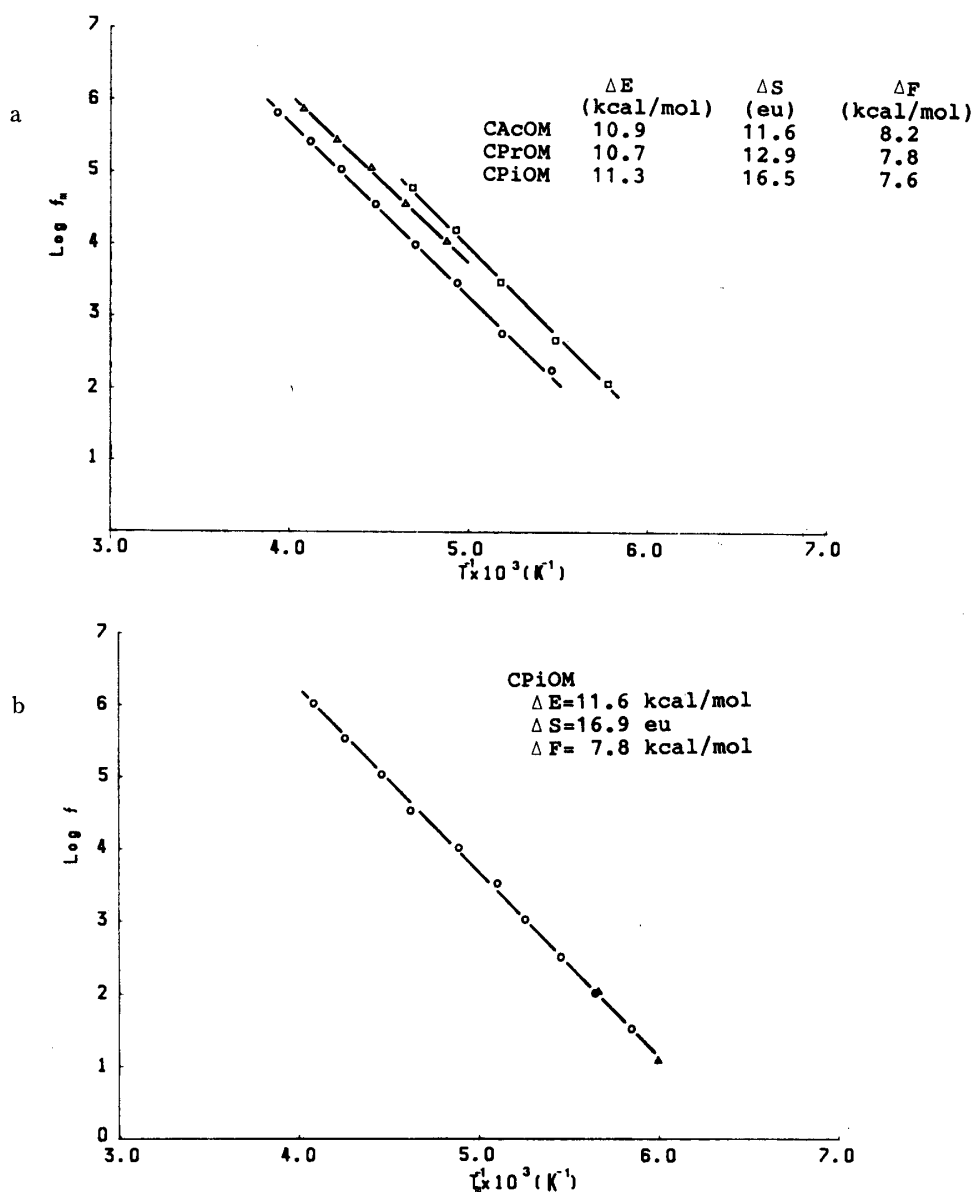


Fig. 9a. Plots of $\log f_m$ vs. $1/T$ for the γ process in CAcOM (\square), CPrOM (\triangle), and CPiOM (\circ).

Fig. 9b. Plots of $\log f$ vs. $1/T_m$ for the γ process in CPiOM. \blacktriangle : from mechanical measurements.

observation means that the γ process for COAs gives a constant ΔE of about 10 kcal/mol and ΔF of 8 kcal/mol. However, a slight difference in ΔS may suggest different freezing points of the side chain micro-Brownian motion for each COA.

The β process for CAcOM appeared as a low frequency shoulder to the predominant γ peak as mentioned before. However, from temperature dispersion data in mechanical measurement for COA with side chain length long enough as decanoate, the β process for such COA is expected to become predominant in frequency dispersion curve. Figure 10 shows ϵ'' vs. $\log f$ curve for CDeOM at temperature between -80°C and 0°C . As is expected, the β process exhibits a peak in the range of -50°C to -30°C . However, the peak seems to become broader in shape with increasing temperature, which suggests that the influence of the γ region is still very large.

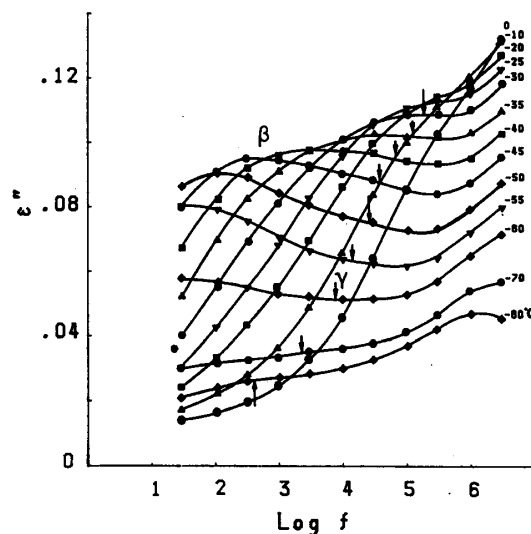


Fig. 10. Frequency dependence of ϵ'' at fixed temperatures between 0°C and -80°C for CDeOM in the β and γ regions.

In order to clarify this point, an attempt was made to resolve the curve for CDeOM at -90°C , in which the β process was removed but instead the γ and δ processes appeared. The result of resolution using Gaussian approximation is shown in Figure 11. Since both the frequency location and the half width of the resolved γ curve at -90°C for CDeOM is comparable to those for CAcOM as shown in the same figure, our resolving method is thought to be reasonable. On the basis of the fact that Arrhenius plots for the γ process for COAs produce lines with the same slope shown in Figure 9a, we can calculate these values above -80°C , using the frequency value at maximum ϵ'' for the γ process at -90°C . In Figure 10, thus estimated γ region is denoted by arrows. In conclusion, even for CDeOM the γ process shows large absorption, causing the broadening of the β peak.

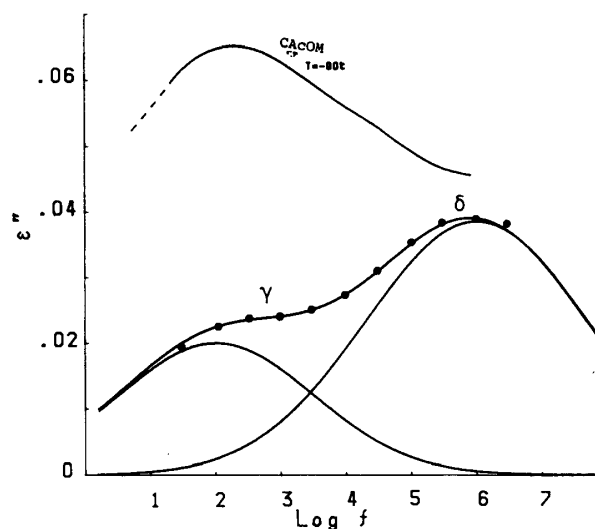


Fig. 11. Frequency dependence of ε'' at -90°C for CDeOM in the γ and δ regions. The curve was resolved by supposing Gaussian distribution form.

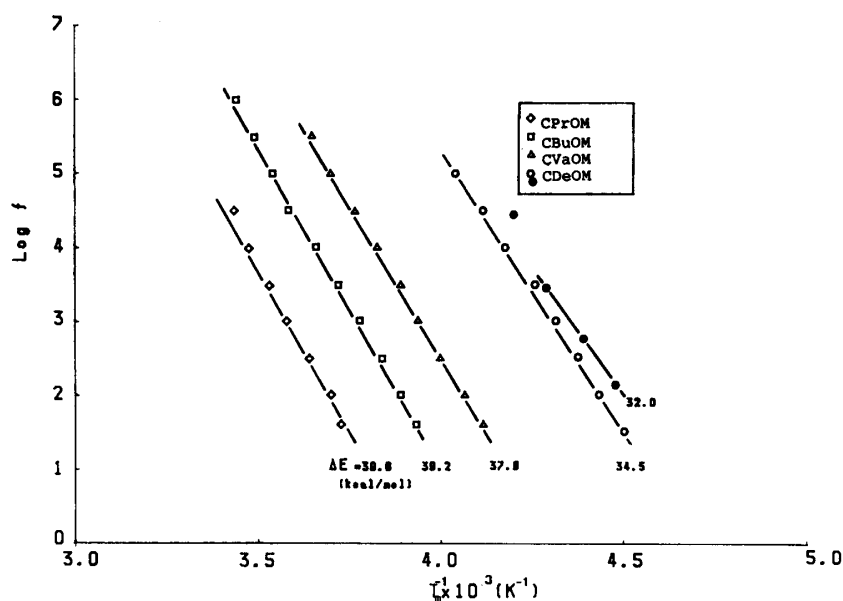


Fig. 12. Plots of $\log f$ vs. $1/T_m$ for the β process in CPrOM, CBuOM, CVaOM, and CDeOM. \bullet : frequency dispersion data.

In contrast, the β process in the absorption curve from temperature dispersion data exhibits large peak as exemplified in Figure 3b. Therefore, we use temperature dispersion data to obtain transition map for the β process, and the results for CPrOM, CBuOM, CVaOM, and CDeOM are illustrated in Figure 12. In the figure, plots for CDeOM from frequency dispersion data (Fig. 10) are also included for reference. It can be recognized that with decreasing the side chain length, lines

Table 1. ΔS , ΔF , and ΔE for the β process of COAs along with other synthetic polymers

	T^{-1} (K $^{-1}$)	ΔS (eu)	ΔF (kcal/mol)	ΔE (kcal/mol)	
The β process of COAs					
CPrOM	.004	97.3	14.8	39.6	
CBuOM	.004	102.8	13.0	39.2	
CVaOM	.004	101.5	11.2	37.0	
CDeOM	.004	103.9	8.0	34.5	
	.004	94.7	7.9	32.0	from the frequency dispersion data
The β process of synthetic polymers					
CTA	.004	0.65	10.6	11.3	C=O group in side chain
PVAc	.004	4.03	8.51	10.0	side chain
PMMA	.003	29.5	13.7	24.2	◇
MCIA	.003	13.2	17.1	22.2	◇
PMA	.004	5.5	6.6	8.5	◇
POM	.003	103.6	14.8	50.0	primary process
PET	.004	12.2	10.3	13.9	COO group
PVC	.004	11.0	12.5	15.7	local mode
PTFH	.004	41.9	6.7	17.6	◇

CTA: cellulose triacetate, PVAc: polyvinyl acetate, PMMA: polymethyl methacrylate, MCIA: methyl- α -chloroacrylate, PMA: polymethyl acrylate, POM: poly oxymethylene, PET: polyethylene terephthalate, PVC: polyvinyl chloride, PTFH: polytetrafluoroethylene.

shift to higher temperature. The ΔE values calculated from the slope ranges from 32.0 to 39.6 kcal/mol, unexpectedly large values compared with typical values related to the side chain motions, even though they are somewhat modified by the γ process. Table 1 summarizes ΔS , ΔF , and ΔE values for the β process of these four kinds of COAs, together with various synthetic polymers. Comparing these values for COA with those for well known synthetic polymers⁴⁾, we can notice the great difference in ΔS value: the former gives ΔS of the order of 100 eu while the latter of the order of 10 eu. An exception to the above is POM. However, the β process of POM is known as due to the micro-Brownian motion of the main chain. This fact supports our previous finding that the β process for COA is initiated by the micro-Brownian motion of the segment along the side chain.

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